

## COLIQUEFACTION OF COAL AND POLYMERS TO LIQUID FUELS

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Coal is our most abundant fossil fuel, but presently supplies only about 24 percent of our total energy. Petroleum provides over 40 percent of our energy, but recently, over one-half of our petroleum demand has been satisfied by imports. This situation constitutes both a strategic and an economic problem which could be partially alleviated by liquefaction of coal. A serious environmental problem is the disposal of polymer wastes such as polyethylene, polystyrene, polypropylene and used rubber tires. Over 22 million tons of plastic wastes are disposed of annually in landfills <sup>(1)</sup> and over 75 percent of discarded used tires are similarly treated (242 million tires in 1992). <sup>(2)</sup> Such waste polymers contain a large fraction of hydrogen which is needed to convert coal to high quality liquids. Coliquefaction of coal and waste polymers has the potential for supplying liquid fuels which could reduce our need on imported crude oil and refined products and at the same time, alleviate an environmental disposal problem.

Several others have studied the coliquefaction of coal with polymeric materials. Only a few will be mentioned here but they are significant relative to our research. W. Hodek combined coal with several plastic polymers with the idea of using coal as a hydrogen donor <sup>(3)</sup>. Using polyethylene, polystyrene, dechlorinated PVC, and "Trabrant resin" in combination with coal, Hodek found coal to be a good hydrogen donor but the reaction rate was low. He also observed that some plastics formed condensation products in his experiments. Both Williams et al. <sup>(4)</sup> and Farcasiu <sup>(5)</sup> utilized rubber tire material to obtain liquid products. Farcasiu used tire rubber in combination with coal and found the quality of liquids produced from coal/polymer combinations higher than for products from thermal coal liquefaction in tetralin. Heptane soluble liquids (oil) represented over 80 percent of the products. This fraction was high in hydrogen (9.7 weight percent) and had low heteroatom content. Williams et al. used only pyrolysis to convert "automotive tyres" to products but nearly 60 percent of the charged rubber material was converted to gases and liquids. Temperatures were relatively high compared with conventional coal liquefaction processes (maximum yields were obtained at 720°C, the highest temperature studied). Molecular weights for the liquid "oil" fell between 100 to 1600 with the maximum number between 300 and 400. As with many pyrolysis processes, higher temperature treatments caused a shift in the molecular weights of the liquids to higher values.

## Experimental

Coliquefaction experiments were conducted in tubing reactors (volume = 29 ml) which were heated in a fluidized sand bath. Reactions were conducted on dry coal and polymer mixtures or pure samples with shaking at 160 rpm and with hydrogen at 2000 psi. Pure polyethylene (PE), polystyrene (PS), and a commingled plastic mixture (mostly high density PE) obtained at a local recycling center were used with a high volatile bituminous coal (DECS-6-Blind Canyon, Utah, obtained from the Penn State Coal Sample Bank). Coal was ground to -100 mesh and plastics were ground to -8+25 mesh. In the case of commingled plastic, the bottles and containers were washed to remove contaminants and labels before size reduction by cutting and shaving. Final size reduction was done by grinding in a kitchen flour mill (stainless steel). Polyethylene and polystyrene were obtained from Aldrich Chemical Company. Analytical data for the coal and commingled plastic are given in Tables 1 and 2. In Table 3, trace element analyses for coal and commingled plastic waste (CPW) are given.

Table 1

Proximate Analysis of Coals and Plastic Waste  
(weight percent, as received)

	Coals DECS-6	DECS-17	Commingled Plastic Waste
Fixed Carbon	47.31	44.9	0.45
Volatile Matter	42.4	45.0	99.7
Ash	5.6	6.3	1.8
Moisture	4.7	3.7	0.06

Table 2.

Ultimate Analysis of Coals and Commingled  
Plastic Waste (weight percent, as received)

	<u>Coals</u>		<u>Plastic Waste</u>
	DECS-6	DECS-17	
Carbon	81.7	82.05	86.3
Hydrogen	6.2	6.2	14.0
Nitrogen	1.6	1.4	.05
Sulfur	0.4	0.44	0.22
Oxygen (by diff.)	10.1	9.94	--

Table 3

Trace Element Analyses for Coals and Commingled Waste Plastic  
(ppm, wt. basis):

	<u>Coals (Blind Canyon, Utah)</u>		<u>Commingled Plastic</u>
	<u>DECS-6</u>	<u>DECS-17</u>	<u>Waste</u>
Cr	6.0	6.0	0.77
Cd	--	--	0.19
Cu	9.0	9.0	--
Ni	<2.0	--	0.4
Pb	--	--	3.2
Zn	4.	3.0	--

Results and Discussion

We have extensively studied the liquefaction of Blind Canyon coal, which has a low pyrite content. Hydroliquefaction of this and other coals of similar rank gives high yields of liquid products at temperatures near 400°C. At higher temperatures, liquid yields decrease as more gases are produced. To determine if coliquefaction could be accomplished experiments were done using different combinations of coal and polyethylene (PE) and coal and polystyrene (PS). In Figure 1 results for total conversion of PE and coal show that highest conversion was obtained at 400°C for PE but little difference was observed for coal/PE at 350 and 400°C. Polystyrene was easier to convert to liquids and gases than was PE as shown in Figure 2. Conversion of PS only at 400°C gave nearly 90 percent conversion. In contrast to polyethylene, polystyrene liquefaction gave highest yields at 300°C (Figure 3). Polystyrene conversion differed from polyethylene in another important respect; gas production. At 300°C a 50:50 mixture of coal and polystyrene gave a conversion of 71.5 percent with most of the product as a liquid (62.3% of the total sample weight). However, at 400°C the conversion dropped to 58%, but the drop in liquids was even greater (to 15%). Coal/polyethylene liquid yields were essentially identical at 350 and 400°C (33.1% and 33.3%, respectively).

Commingled plastic waste (CPW) contained some polystyrene, and other plastics, but the most abundant polymer in this waste was high density polyethylene (HDPE). CPW was composed of many large and small drink bottles, soap containers, prescription drug containers, etc. Colors included black, transparent, red, orange, green and blue. This material was by far the most difficult to convert to liquids soluble in THF. As shown in Figure 4 the conversion values for commingled plastic was much lower than for either PS or PE. From the trend shown at different temperatures it appears that higher temperatures may be required to obtain satisfactory liquid yields. Other results not shown in Figure 4 have been obtained for 50/50 coal/CPW at 450 and 500°C. At these higher temperature, total conversions were 28 percent with liquid yields of 23 percent at 450°C and 35 percent with a liquid yield of

26 percent at 500°C. CPW/coal/waste rubber tire material (WRT) were reacted at 450°C (33/33/33) and gave only slightly higher conversion and liquefaction (36 percent and 32 percent, respectively). Even higher temperatures and/or suitable catalysts will obviously be required to obtain higher conversion and liquefaction values.

From work by others using waste rubber tire material (WRT) it has been observed that high yields of liquids and gases can be obtained. We also reacted WRT with coal and with coal/CPW. Table 4 gives results at 350°C using a catalyst, ammonium tetrathiomolybdate (1% of total feed weight) for coal only and mixtures of coal and WRT. Although simple mechanical addition of the catalyst was no better than hydroliquefaction without catalyst, impregnation from aqueous solution improved the liquefaction (from 56% to 79% for 60/40 coal/WRT).

Table 4

Results for hydroliquefaction of Blind Canyon Coal (DECS-17 and Waste Rubber Tire Material Using 1% (weight % of total feed) Ammonium tetrathiomolybdate. (Temperature = 350°C)

% Coal in feed	% WRT in feed	Catalyst addition	Yields, (wt. %)	
			Liquids (THF Sol.)	Gas
100	0	none	36	
2				
60	40	Impregnated	79	2
50	50	Impregnated	65	2
50	50	Mechanically added	55	1
60	40	none	56	2

Reaction of coal and plastic materials, especially commingled plastic waste (CPW) has so far given only marginal results. Even for relatively long reaction times (1 hour) and temperatures up to 500° C liquid yields are less than we have obtained for hydroliquefaction of coals. Further work and characterization of the liquid products will be necessary to improve the conversion of coal/plastic streams to high quality liquid products.

#### Summary

Hydroliquefaction of coal, polyethylene, polystyrene and waste rubber tire material individually gives good conversion and liquefaction yields. Combinations of these materials gave less satisfactory results as far as liquid yields were concerned. Catalyst application (molybdenum) enhances the reaction to increase liquid yields and to produce higher quality liquids.

### Acknowledgement

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### References

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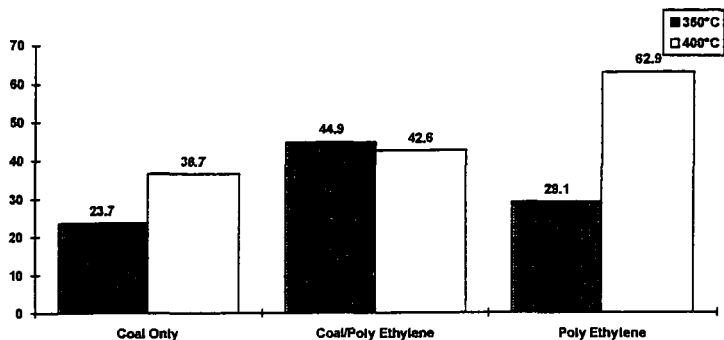


Figure 1. Coliquefaction yields for Blind Canyon Coal and PE (50/50) at two temperatures. Values are total conversion.

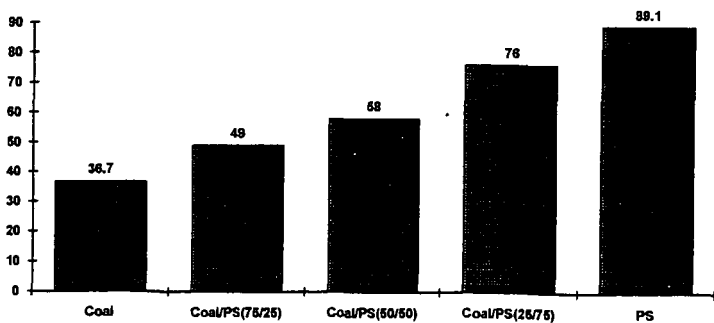


Figure 2. Coliquefaction conversion (liquids + gases) for Blind Canyon Coal and PS at 400°C (weight percent).

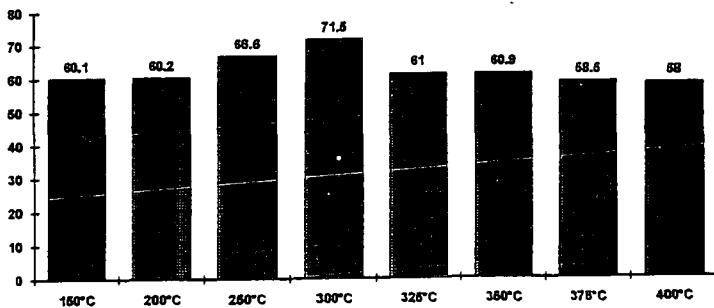


Figure 3. coliquefaction yields (liquids + gases, weight percent) for Blind Canyon Coal and PS (50/50) different temperatures.

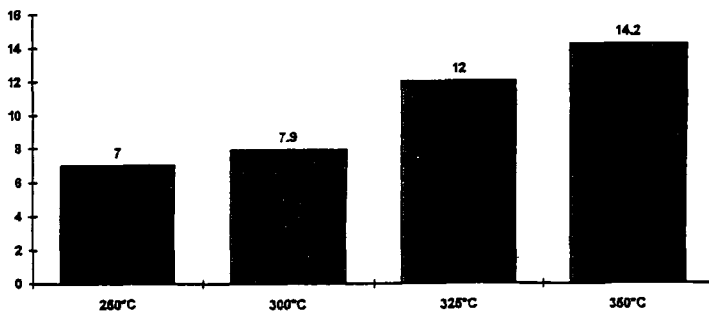


Figure 4. Coliquefaction yields (liquids + gases, wt percent) for Blind Canyon Coal and Commingled Plastic waste (50/50) at different temperatures.